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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Edouard A. Mamedov
 Kathleen A. Bethke
 Shahid N. Shaikh
 Armando Araujo
 Neeta K. Kulkarni
 Andrei Khodakov

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For: Catalyst Compositions for the Ammoxidation of Alkanes and
Olefins, Methods of Making and of Using Same

Mail Stop Non-Fee Amendment
Commissioner for Patents
P.O.Box 1450
Alexandria, Virginia 22313-1450

DECLARATION UNDER 37 CFR §1.132

Edouard A. Mamedov, says that:

I am a research scientist and team leader for SABIC Technology Center, SABIC Americas, Inc. My educational background is as follows: I hold a degree of a Bachelor of Science in Chemistry from Baku State University received in 1964 and a degree of a Doctor of Philosophy in Chemistry from the Institute of Catalysis received in 1971.

My duties involve research in the field of propane ammoxidation to acrylonitrile, including catalysts such as those disclosed in U.S. patent no. 5,008,427. I have worked in the

field of ammoxidation catalysis for over twenty-five years, specializing in propane ammoxidation to acrylonitrile for the last four years. I am the author or co-author of seventeen articles and one book on alkylaromatics ammoxidation and have approximately three U.S. patents naming me as an inventor or co-inventor in this field. In view of my qualifications as specified above, I consider myself to be an expert in the art of ammoxidation catalysis, and specifically, propane ammoxidation to acrylonitrile.

I have read the above-identified patent application and the Office Action dated July 2, 2003, including the cited reference U.S. Patent no. 5,008,427.

Under my supervision, the following laboratory experiments were carried out. The first example below was a duplication of Example 6 of the present patent application having a nominal composition $\text{VSb}_9\text{Ti}_6\text{O}_x$:

Under vigorous stirring, 8.68 g TiCl_4 was added in 300 mL of de-ionized water at room temperature via dropping funnel. An exothermic reaction occurred, and a white precipitate was formed. After addition of TiCl_4 , pH was adjusted to 9.0 with 30% NH_4OH to obtain white slurry. 15.4 g SbCl_3 was dissolved in 30 mL diluted nitric acid with a HNO_3 to H_2O volume ratio of 1:3 to obtain syrupy slurry. This slurry was added to the

pale-yellow solution of 0.877 g NH_4VO_3 in 50 mL of de-ionized water at 90°C . The heat under the suspension was turned off, and the slurry was stirred for 30 minutes. The pH of the greenish-white slurry was adjusted to 8.5 with 30% NH_4OH . This alkaline slurry was then added to the above-prepared slurry of TiCl_4 and stirred for an hour. The precipitate was filtered and transferred to a porcelain dish, dried and calcined in air under the following ramp conditions: room temperature to 120°C at $5^\circ\text{C}/\text{min}$, held for 5 hours; 430°C at $20^\circ\text{C}/\text{min}$, held for 4 hours; 650°C at $20^\circ\text{C}/\text{min}$, held for 6.5 hours. The calcined material was cooled down to room temperature, ground to fine powder, pressed and sieved to 18-30 mesh.

The second example below was a duplication of Example M of U.S. Patent no. 5,008,427 having an empirical composition $\text{VSbTi}_{6.75}\text{O}_x$:

27.58 g of V_2O_5 powder was slurried in 400 cc of water in a 1.0 liter beaker. While vigorously stirring, 70 g of a 30% H_2O_2 solution in water was slowly added and the V_2O_5 began to dissolve. In this step the peroxovanadium ion forms. After about 15 minutes some undissolved V_2O_5 remained, and another 70 g of the 30% H_2O_2 solution was added with continued stirring. The

final dispersion was a red solution with some orange flocculent solids.

44.2 g of powdered Sb_2O_3 was added to the foregoing dispersion. The mixture was stirred for about 4 hours with heating in order to reduce the volume by evaporation of water. During this time, the slurry formed gradually, turned to a deep blue-green, then finally to a blackish green. The additional element Ti was introduced as a TiO_2 sol. 164 g of TiO_2 was added in the slurry resulting from the reaction of the vanadium compound and the antimony compound. When the mixture could no longer be stirred, it was dried in an oven for about 16 hours at 100°C . Thereafter, it was calcined for 8 hours at 650°C ., cooled and then crushed and sieved to 20-35 mesh. The calcined material was very hard.

A portion of this catalyst was activated by calcining for 1 hour at 950°C . A portion of the activated catalyst was washed with water in a Soxhlet extractor for several hours until the wash water appeared colorless. The washed catalyst was then dried by heating at about 100°C . for about 3 hours.

Both samples were analyzed by powder X-ray diffraction (XRD) on the same instrument. As is seen from Table 1 and attached XRD patterns, the reference catalyst contained rutile-type VSbO_4 phase which indicates that vanadium and antimony sites are not isolated in a matrix of metal oxides. The claimed catalyst does not contain VSbO_4 . The distinctive peaks designated by "x" in the attached XRD patterns are not present in the claimed catalyst. These XRD results demonstrate that the claimed catalyst has a different composition from that of the reference catalyst in that the vanadium and antimony sites are isolated in a matrix of metal oxides.

Both catalyst samples were tested for propane ammoxidation to acrylonitrile under the same conditions. The results of this comparative study are presented in Table 1.

Table 1

Catalyst formulation	Preparation method	Phases	τ^1 (s)	T^2 ($^{\circ}\text{C}$)	Propane ³ Conv. (%)	ACN Sel. (%) ⁴
$\text{VSbTi}_{0.75}\text{O}_x$	5,008,427 Example M	TiO_2 , VSbO_4	0.3	475 500	6.7 9.7	14.0 21.3
			0.5	475 500	14.9 18.5	19.6 25.8
$\text{VSb}_2\text{Ti}_6\text{O}_x$	10/036,866 Example 6	TiO_2 , Sb_2O_3	0.5	475 500	9.6 11.4	48.2 51.0
			2.0	475 500	13.8 17.7	48.5 48.0

- ¹ Contact time, seconds
- ² Reaction temperature, degrees Celsius
- ³ Feed $C_3H_8/NH_3/O_2/He = 18/8/15/59$, volume %
- ⁴ Acrylonitrile selectivity based on propane

Product selectivity in oxidation reactions is related to hydrocarbon conversion. To reduce this effect, the selectivities of different catalysts are usually compared at similar conversions. Under the conditions listed in Table 1, the reference catalyst gave 19.6% selectivity to acrylonitrile at propane conversion 14.9% for a contact time of 0.5 sec and at a temperature of 475°C. Comparison of reference catalyst with the claimed catalyst shows that the latter is more selective with respect to acrylonitrile production. For instance, the claimed catalyst displayed 48.2% selectivity to acrylonitrile at conversion 9.6% at the same process conditions. For a contact time of 0.5 sec and at a temperature of 500°C, the reference catalyst gave 25.8% selectivity at 18.5% conversion compared to 51.0% selectivity at 11.4% conversion for the claimed catalyst. It is believed that this significant difference in acrylonitrile selectivity is related to the structural differences of the catalysts as confirmed by the XRD results discussed above.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made herein on information and belief are believed to be true; and further that all statements herein were made with the knowledge that willful false statements and the like so made are punishable by fine or

SERIAL NO. 10/036,866

PATENT APPLICATION

MAMEDOV, BETHKE, SHAIKH, ARAUJO, KULKARNI, KHODAKOV

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imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

E. Mamedov

Signature

8/28/03

Date